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PHOTO-INDUCED CHARGE SEPARATION IN CARBAZOLE-CONTAINING BILAYER MEMBRANE IN THE PRESENCE OF VARIOUS ELECTRON ACCEPTORS[1)]

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Double-chain ammonium amphiphile with carbazole moiety affords spontaneous assemblage, bilayer vesicles, in aqueous solution. Laser-excitation of aligned carbazole units in the bilayer liberates electron, which lead to long-living charge-separated states (ca. 50 μs-5 ms) in the presence of appropriate electron acceptors.

Photo-induced electron transfer reactions in organized molecular assemblies are currently of interest as a method of solar energy conversion and storage.[2)] Various molecular organizates including micelles,[3)] vesicles,[4)] and poly electrolytes[5)] were used as microscopically heterogeneous phase boundary that control the photo-redox reactions, i.e., electron transfer quenching and recombination of the intermediate photo-products. In the presence of these charged phase boundaries and the hydrophobic inner core, electrostatic force acting on the charged photo-products[6)] and the abrupt change of hydrophobicity of the redox species[7)] are operative in controlling the charge separation process. Novel means of retarding the recombination reaction of the photo-redox products has been recently introduced by the use of amphipathic electron acceptors. In these systems, the charge separation proceeds via electron-exchange between the neighboring acceptors aligned on the surface of molecular assemblies.[3,8)]

Aligned electron donors in the interior of molecular assemblies are also useful for photoinduced charge separation as it will be discussed in this paper. In this case, the charge separation may proceed via hole-exchange between the neighboring donors. Carbazole units were used as the electron donor, because carbazole ring is known to be a principal chromophore in photo-conducting polymers in which hole transfer is a major electron conducting process,[9)] and its photophysical properties have been studied extensively.[10,11)]

The molecular structure of amphiphiles and electron acceptors employed in the present experiments is shown in Fig. 1. Double-chain ammonium amphiphile with carbazole moiety (abbreviated to $2C_{12}CzC_4NB$) affords molecular bilayer structure with the molecular weight of 10^8 Dalton on sonication of aqueous solution[12)] (critical assembly concentration, $< 1\times10^{-5}$ M (1 M=1 mol dm^{-3})). A Lambda Physik EMG-100 excimer laser (XeF excimer laser, 351 nm, 15 ns, max. 60 mJ/pulse) was used for laser flash photolysis.

On laser photolysis of the aqueous solution containing $2C_{12}CzC_4NB$ and various

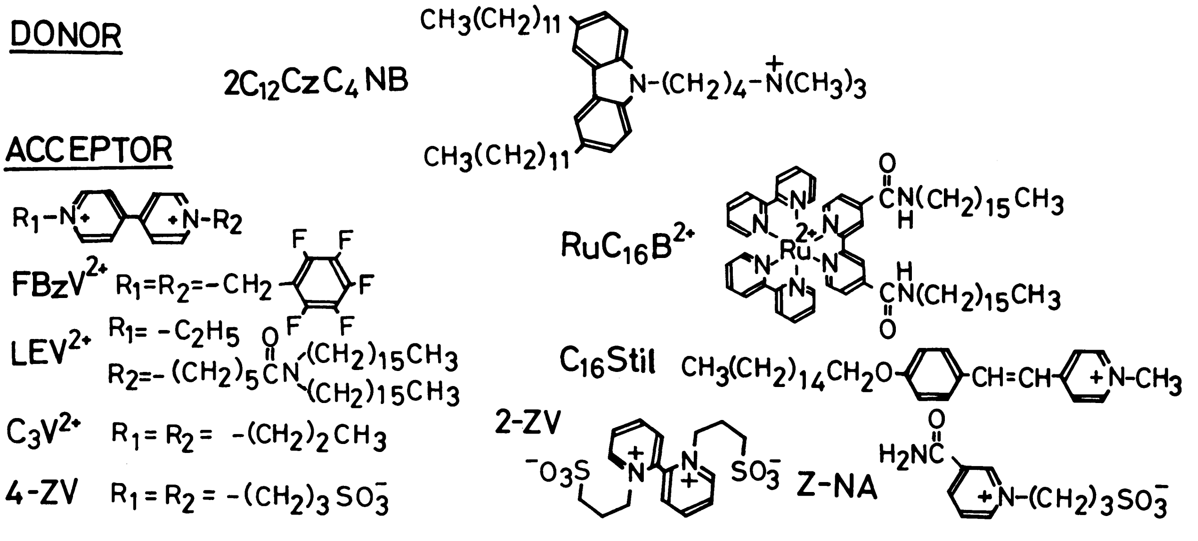

Fig. 1. Structure and abbreviation of donor and acceptors.

electron acceptors (A), redox pairs were generated and the reverse electron transfer was remarkably suppressed. Lifetime of the following charge separated states covered time domain from µs to ms as described below:

$$\mathrm{Cz}^{*} + \mathrm{A}\ (\text{acceptor}) \rightleftarrows \mathrm{Cz}^{+\cdot} + \mathrm{A}^{-\cdot} \qquad (1)$$

A typical example of the transient absorption spectra is shown in Fig. 2. When viologens are acceptors, the concentration of the initially produced $\mathrm{Cz}^{+\cdot}$ (detected at 780 nm) agreed with that of $\mathrm{A}^{-\cdot}$ (detected at 605 nm). Both of the transient absorption bands at 780 and 605 nm gave the same decay profiles. Except for the viologens, the spectra of the reduced acceptor were not observed due to the small molecular extinction coefficient in visible region. Decay kinetics were studied by the use of absorbance at 780 nm alone. In the case of $\mathrm{RuC_{16}B^{2+}}$, the spectra of its reduced form, $\mathrm{RuC_{16}B^{+}}$ with λ max. at 515 nm, were observed.

The above acceptors are divided into two types; Type I ($\mathrm{LEV^{2+}}$, $\mathrm{C_{16}Stil}$, and $\mathrm{RuC_{16}B^{2+}}$) and Type II (Z-NA, 2-ZV, 4-ZV, $\mathrm{C_3V^{2+}}$, and $\mathrm{FBzV^{2+}}$). Type I acceptors are amphiphilic compounds, which are expected to be incorporated into the surface of bilayer membrane. Type II acceptors stay in the bulk aqueous phase because of the highly hydrophilic structure. Correspondingly 80% and 95% of the luminescence from Cz was quenched by $\mathrm{LEV^{2+}}$ and $\mathrm{C_{16}Stil}$, respectively. While no quenching was observed with $\mathrm{C_3V^{2+}}$, 4-ZV, 2-ZV, Z-NA, and $\mathrm{FBzV^{2+}}$ under the experimental conditions. Clear distinction between Type I and Type II acceptors was also observed in the decay rate of transient absorptions. As to Type I acceptor, extremely rapid decay at the first stage (< 5 µs after the photolysis) was followed by rather

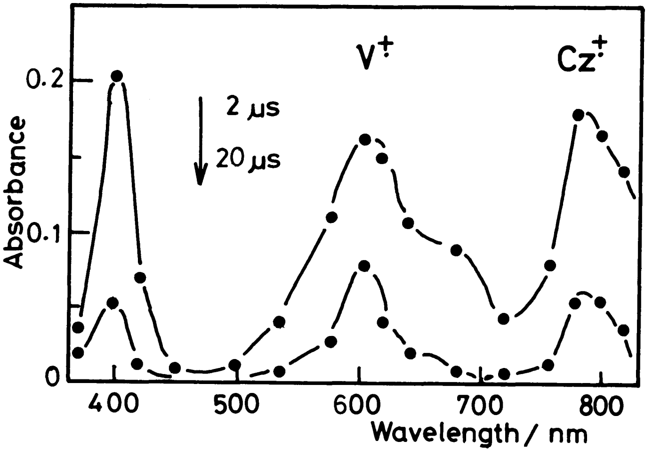

Fig. 2. Transient absorption spectra of $\mathrm{2C_{12}CzC_4NB}$ and $\mathrm{LEV^{2+}}$ system.

$[\mathrm{2C_{12}CzC_4NB}]$ = 200 µM, $[\mathrm{LEV^{2+}}]$= 20 µM.

Table 1. Rate constant of back-electron-transfer from reduced acceptor in carbazole bilayer membrane system

Acceptor	$E_{red.}$/V vs.NHE	$k_b/M^{-1}s^{-1}$ at 780 nm	$k_b/M^{-1}s^{-1}$ at 605 nm	Apparent lifetime of charge-separated state
LEV^{2+}	-0.21	1.08×10^{10}	8.85×10^{9}	≈ 50 μs
$FBzV^{2+}$	-0.24	1.90×10^{8}	1.93×10^{8}	≈ 2 ms
4-ZV	-0.37	1.02×10^{8}	1.06×10^{8}	≈ 5 ms
C_3V^{2+}	-0.42	2.29×10^{8}	3.28×10^{8}	≈ 2 ms
2-ZV	-0.68	1.96×10^{9}	——	≈ 0.5 ms
$C_{16}Stil$	-0.74	1.10×10^{10}	——	≈ 50 μs
Z-NA	-0.99	1.15×10^{10}	——	≈ 50 μs
$RuC_{16}B^{2+}$	-1.26	9.95×10^{9}	——	≈ 50 μs

$[2C_{12}CzC_4NB]$ =200 μM, $[C_3V^{2+}]=[4\text{-ZV}]=[2\text{-ZV}]=[Z\text{-NA}]$=20 mM, $[FBzV^{2+}]$=10 mM, $[LEV^{2+}]=[C_{16}Stil]=[RuC_{16}B^{2+}]$=20 μM, $\varepsilon(Cz^{\dot{+}})$ at 780 nm =9400 $M^{-1}cm^{-1}$.

slow decay at the second stage covering time domain later than 10 μs. The decay of the first stage could not be analyzed by either the first order or the second order kinetics, while the decay of the second stage followed the second order kinetics. In the case of Type II acceptors, on the other hand, the decay followed the second order kinetics from the beginning. The rate constants (k_b) as calculated by the use of decay components following the second order kinetics are summarized in Table 1. The k_b-values are also plotted against the ΔG-values of the back electron transfer reaction (Fig. 3). In the case of Type II acceptors, the k_b-values decrease with ΔG-values. The apparent lifetime of charge-separated states could be extended up to 5 ms (4-ZV, Table 1). The k_b-values for Type I, on the other hand, are almost the same (10^{10} M^{-1} s^{-1}) and irrespective of the ΔG-values. The apparent lifetime of the charge separated state is rather short (≈50 μs), but it is definitely longer than expected lifetime for donor-acceptor system at close distance.

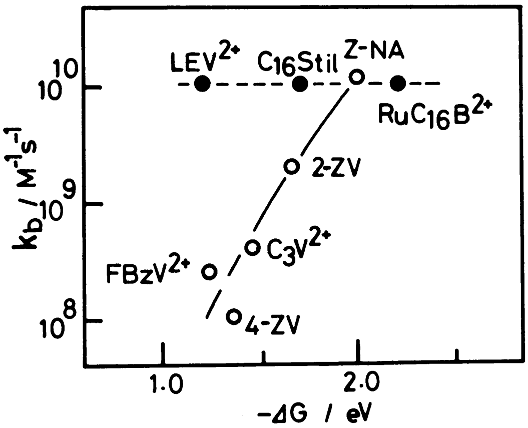

Fig. 3. k_b vs. the difference of redox potential (ΔG) between $Cz^{\dot{+}}$ and various acceptors.

The details of the photo-induced electron transfer process from excited carbazole to various acceptors are not fully resolved at present. But it appears that different laser intensity dependence of charge separation yield is observed with the two types of acceptors (Fig. 4). In the case of Type II, viologen radical concentration at 5 μs after laser irradiation was proportional to the square of laser intensity upto ca. 25 mJ. It may be that the electrons photo-ejected from Cz via biphotonic process are captured by Type II acceptors in bulk aqueous solution. The spectra of hydrated electron, however, could not be detected in the $2C_{12}CzC_4NB$ bilayer system without quencher. As to Type I acceptors, on the other hand, the radical concentration quickly came to a plateau, and became independent of the laser intensity after 10 mJ. In this case, direct quenching of Cz-singlet state via electron transfer to Type I acceptor in the same membrane may be the primary process of the charge separation.

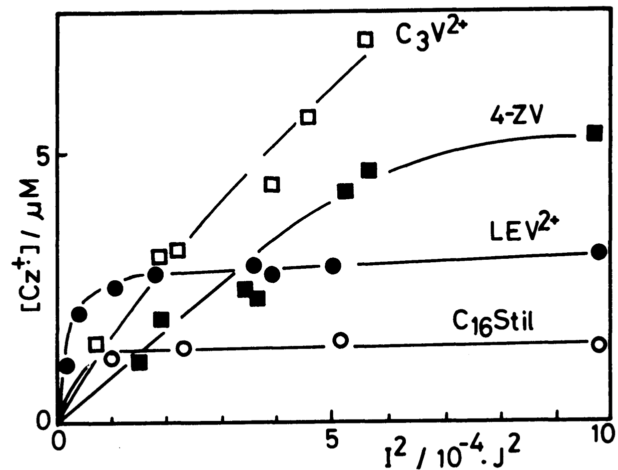

Fig. 4. Effect of laser intensity (I^2) on the $Cz^{\dot{+}}$ concentration at 5 µs after photolysis. $[2C_{12}CzC_4NB]$=200 µM, $[C_3V^{2+}]$= [4-ZV] =20 µM, $[LEV^{2+}]$= $[C_{16}Stil]$ =20 µM.

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